VUV–UV 5d–4f interconfigurational transitions of Nd³⁺ in BaMgF₄ ferroelectric crystals

M. Trevisani^a, K.V. Ivanovskikh^b, M.O. Ramírez^c, P. Molina^c, E.G. Villora^d, K. Shimamura^d, L.E. Bausá^c, M. Bettinelli^{a,*}

^a Luminescent Materials Laboratory, Department of Biotechnology, University of Verona, and INSTM, UdR Verona, Strada Le Grazie 15, 37134 Verona, Italy

^b Institute of Physics and Technology, Ural Federal University, Ekaterinburg 620002, Russia

^c Dept. Física de Materiales and Instituto Nicolás Cabrera, Universidad Autónoma de Madrid, 28049 Madrid, Spain

^d National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

ARTICLE INFO

Article history:

Received 9 October 2013

Received in revised form

19 February 2014

Accepted 25 February 2014

Available online 13 March 2014

Keywords:

Nd³⁺

BaMgF₄

Single crystal

5d–4f Luminescence

VUV spectroscopy

Synchrotron radiation

ABSTRACT

BaMgF₄ single crystals doped with Nd³⁺ are of great interest as possible active media for VUV–UV and mid-IR all solid-state lasers. The luminescence spectroscopy and the excited state dynamics of these crystals are investigated for the first time upon VUV excitation using synchrotron radiation. The material shows fast Nd³⁺ 5d–4f emission upon direct VUV excitation into Nd³⁺ 5d levels. The decay kinetics of the Nd³⁺ 5d–4f emission in this host lattice upon direct VUV excitation of 5d levels is characterized by a lifetime of about 14 ns with no significant rise after the excitation pulse. No significant temperature dependence of the lifetime is observed within the range 8–300 K.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

BaMgF₄ (BMF), one of the few ferroelectric fluorides reported up to now, is a nonlinear crystal which exhibits an extraordinary transparency range extended from the deep UV (~125 nm) to the mid-infrared (~13 μm) [1]. This constitutes an exceptional window for the observation of optical processes or transitions not possible in other systems, and offers a unique chance to fabricate optical devices operating in the UV and mid-IR, where other nonlinear materials cannot be used. Regarding its photonic applications, frequency conversion processes in both visible and UV spectral region have been recently reported by using different schemes. Namely, a collinear second harmonic generation (SHG) as well as conical Cerenkov SHG processes have been recently achieved by using 1D and 2D ferroelectric domain structures, respectively. Further, a very efficient UV third harmonic generation (THG) at 385 nm has been also demonstrated by means of a $\chi^{(3)}$ process [2,3]. In this context, the use of this BMF ferroelectric crystal as a host matrix for optically active ions appears as a very interesting subject [4–6]. In the last years there has been an

increasing interest in the study of the parity-allowed 5d–4f transitions of various trivalent rare earth ions (RE³⁺) incorporated in wide band-gap host lattices for potential applications in the field of scintillators, UV and VUV phosphors and lasers [7–9]. The VUV–UV broad band emission resulting from the interconfigurational 5d–4f transitions of appropriately chosen RE³⁺ ions, combined with the use of the compact pumping sources, may provide the possibility to realize coherent and tunable VUV–UV radiation sources. Among these dopant ions, Nd³⁺ ion seems a particularly promising candidate in the development of potential self-frequency converted all solid-state lasers operating in the UV and VUV and mid-IR spectral region. The potential use of Nd³⁺-doped BMF single crystals for self-frequency-doubling lasers has already been documented in a recent paper [10], where the spectroscopy properties of this material have been thoroughly investigated under excitation in the near IR region. However, to the best of our knowledge the spectroscopic characteristics of the interconfigurational 5d–4f transitions of Nd³⁺ ion in BMF have not been reported in literature so far, although the Nd³⁺ laser action in VUV–UV spectral region based on the 5d–4f transitions has already been demonstrated in other similar fluoride single crystals such as LaF₃ and LiYF₄ [11,12].

In this contribution we investigate the 5d–4f transitions of Nd³⁺ ions in BMF crystals upon selective excitation with synchrotron

* Corresponding author. Tel.: +39 045 8027902.

E-mail address: marco.bettinelli@univr.it (M. Bettinelli).

radiation in the VUV–UV region in order to understand the basic spectroscopic and dynamical properties of the higher excited Nd^{3+} dopant states, therefore exploring the possibility of obtaining tunable VUV–UV solid state optical devices.

2. Experimental and structural details

Luminescence measurements were carried out at the SUPER-LUMI station of HASYLAB (Hamburg, Germany) using the synchrotron radiation (SR) from the DORIS III storage ring as excitation source. For the selective excitation and measurements of excitation spectra in the range of 3.7–19 eV a 2 m monochromator in McPherson mounting with a resolution of 3.2° was used. The detection of the luminescence was performed with a 0.3 m ARC SpectraPro-308i monochromator equipped with a high-speed R3809U-50S (Hamamatsu) microchannel plate detector. The measurements were performed at the reduced (two) bunch mode of the storage ring that allowed better time separation for time-resolved spectroscopic measurements that was performed employing time-correlated single photon counting (TCSPC) technique. The time-resolved spectra were recorded within two time windows (TWs): 3–35 ns (fast TW) and 248–430 ns (slow TW) relative to the beginning of the SR pulse. The time-integrated spectra were recorded detecting emission signal within the whole time period of 480 ns available between SR pulses. The measurements were performed in the ultra-high-vacuum chamber ($\sim 10^{-9}$ mbar) in the temperature range 8–300 K. The excitation spectra were corrected for the wavelength-dependent variation of the SR intensity using a sodium salicylate signal. The samples were mounted on a sample holder regardless to the orientation of crystallographic axes relative to the polarization of SR beam.

BMF crystallizes in the orthorhombic system, with space group $\text{Cmc}2_1$ [13]. The room temperature structure is non-centrosymmetric, with 4 molecules per unit cell. The Ba^{2+} ion has a coordination number of 9, while Mg^{2+} is octahedrally coordinated. The ionic radius of Nd^{3+} is much closer to the one of Ba^{2+} , and therefore the dopant ion was proposed to enter into the Ba^{2+} sites [10]. The charge compensation required by Nd^{3+} doping could be achieved by cation vacancies or by interstitial F^- ions [14].

For this research two Nd^{3+} doped BaMgF_4 single crystals were grown using the Czochralski technique under CF_4 atmosphere [1]. One of the samples contained 0.02 mol% of Nd^{3+} ions relative to Ba^{2+} . Another sample contained 0.02 mol% of Nd^{3+} ions and 0.15 mol% of Na^+ . The latter was used for charge compensation. The Nd^{3+} and Na^+ concentrations in the crystals were measured by inductively coupled plasma (ICP).

3. Results and discussion

The time-integrated emission spectrum of BMF:Nd^{3+} , recorded in the UV spectral region (200–430 nm) at room temperature (RT) upon VUV intra-centre excitation ($\lambda = 164$ nm), is dominated by a strong double band extending from 210 to 300 nm and a weaker and unresolved band centered at about 370 nm (Fig. 1). These emission features, which were found to be characterized by a fast decaying emission signal, are identified as parity-allowed inter-configurational transitions from the lowest $4f^25d^1$ state to the multiplets belonging to the ground $4f^3$ electronic configuration of Nd^{3+} dopant ions. In particular, the band peaking at 226 nm is assigned to the transition to the 4F_J ($4f^3$) states, whilst the one peaking at 257 nm is assigned to the transition to the 4G_J ($4f^3$) states [15]; finally, the weak and unresolved band located at 370 is attributed to the transitions to the 4D_J ($4f^3$) states [15]. We point

Fig. 1. RT time-resolved and time-integrated emission spectra of BMF:Nd^{3+} crystal upon excitation at 164 nm. Inset shows the decay curve recorded monitoring Nd^{3+} emission upon intra-centre excitation at 300 K.

out that we were unable to record emission features related to the transition to the ground multiplet 4I_J ($4f^3$), which are expected to be located at about 175–185 nm for Nd^{3+} ion in a fluoride host. The reason for this were technical issues during our beamtime. Nevertheless, it is reasonable to state that the VUV emission features related to transitions to 4I_J ($4f^3$) terminating states are the strongest ones in the 5d–4f emission spectrum of BMF:Nd^{3+} . This was observed in many different oxide and fluoride hosts and it is well proven by calculation of oscillator strengths for Nd^{3+} 5d–4f transitions (see [15–20] and references therein). The measurements were also carried out at low temperature (8 K) under the same experimental conditions. The low temperature spectrum did not reveal any noticeable difference compared to the spectrum recorded at RT (Fig. 2).

Fig. 3 represents time-integrated and time-resolved excitation spectra recorded monitoring Nd^{3+} 5d–4f emission at RT ($\lambda_{\text{em}} = 258$ nm). The time-integrated spectrum is characterized by a strong structured feature spread in the range 135–175 nm with the lowest energy maximum at 165 nm. The feature is predominantly formed by a signal detected in the fast TW and is assigned to the transitions from the ground state $^4I_{9/2}$ to the levels belonging to the $4f^25d^1$ configuration of Nd^{3+} . On the basis of experimentally observed spectral position of the first excitation maximum for Ce^{3+} in BMF when substituting the Ba^{2+} sites (~ 260 nm, $38,460 \text{ cm}^{-1}$) [6,22,23], which agrees with the theoretical calculation [24], and the energy difference between the first 4f–5d transition of Nd^{3+} and Ce^{3+} ($22,700 \text{ cm}^{-1}$ [26]), we estimate a first 4f–5d excitation maximum to be at about 164 nm ($61,160 \text{ cm}^{-1}$). This is in excellent agreement with our experimental data. On the other hand, the spectroscopic data documented in Refs. [6,22,23] allow estimating a Stokes shift for Ce^{3+} 5d–4f emission in BMF that is about 4400 cm^{-1} . Assuming that the Stokes shift for the rare earth ions having very close ionic radius should be pretty much the same, we can approximately locate the first emission maximum related to the ground $^4I_{9/2}$ ($4f^3$) terminating state as ~ 176 nm ($56,760 \text{ cm}^{-1}$).

The excitation peak at 125 nm (9.93 eV) is well pronounced in the spectrum recorded within slow TW. In fact, excitation of BMF:Nd^{3+} crystal at about 125 nm or at shorter wavelengths gives rise to an emission spectrum which is virtually lacking any features related to Nd^{3+} 5d–4f transitions and it is composed of a nearly symmetrical broad band extending from about 210 to 475 nm and centered near 310 nm (Fig. 4). This emission band is dominated by

Fig. 2. Time-resolved and time-integrated emission spectra of BMF:Nd³⁺ crystal upon excitation at 164 nm at 8 K. Inset shows the decay curve recorded monitoring Nd³⁺ emission upon intra-centre excitation at 8 K.

Fig. 4. RT time-resolved and time-integrated emission spectra of BMF:Nd³⁺ crystal upon excitation at 125 nm.

Fig. 3. RT time-resolved and time-integrated excitation spectra of BMF:Nd³⁺ and Na⁺ co-doped BMF:Nd³⁺ crystals recorded monitoring Nd³⁺ 5d–4f emission at 258 nm.

a signal detected within slow TW. A nature of this emission band as well as the excitation feature at 125 nm is most likely connected with intrinsic electronic excitations in BMF.

To our data, BMF is lacking a systematic spectroscopic study of the host absorption characteristics. However, some publications report transmission and excitation spectra of undoped BMF which suggest that fundamental absorption edge of the host should start at about 9.5 eV [1,21,22]. As long as BMF represents a BaF₂–MgF₂ system, it should keep carrying some electronic properties of the binary components (although the crystal structure of BMF is different from BaF₂ and MgF₂) including a large band gap which is about 11 eV for BaF₂ [27] and 12.8 eV for MgF₂ [28]. This is consistent with theoretical calculation [25] which proposes the beginning of interband transitions in BMF to begin at about 10.3 eV. The optically recorded beginning of fundamental absorption can be connected with excitonic absorption. In the case of binary fluorides characterised by a strong exciton–phonon interaction this implies an observation of broad (up to 1.5–2 eV)

excitonic features in excitation or absorption spectra [29]. On this basis, the observed feature in the excitation spectrum at 125 nm (Fig. 3) can be connected with excitonic absorption of BMF. In turn, the 310 nm emission band observed upon excitation into this feature (Fig. 4) can be tentatively assigned to self-trapped exciton (STE). This is worth comparing with position of a STE emission band in BaF₂ (~307 nm) and MgF₂ (~387 nm) (see [29] and references therein). Nonetheless, based on our experimental results, a defect nature for the 310 nm emission band cannot be ruled out. The unambiguous assignment of this emission requires further investigation in undoped BMF crystals being beyond the scope of this work.

Nevertheless, it is clear that energy transfer from the host electronic excitations to Nd³⁺ 5d states is not observed in BMF:Nd³⁺ crystal. This can be due to the fact that energy of relaxed (self-trapped) exciton in BMF is too low to excite 4f–5d transitions in Nd³⁺ that requires energy higher than 7.1 eV. An efficiency of recombination energy transfer depends on absolute location of ground state of the dopant ion [30]. Unfortunately, to the best of our knowledge an information on absolute location of rare earth energy levels in BMF is not available in literature. It is known, however, that the energy difference from the top of the valence band to the Nd³⁺ 4f³ ground state is about 3 eV in CaF₂ [31], 2.5 eV in BaF₂ [32], 3.5 eV in K₃YF₆ [33], 2.7 eV in NaLaF₄ [34] that allows supposition that the Nd³⁺ ground state in BMF is likely located at quite high energy too. The latter prevents more-or-less effective capture of (self-trapped) holes from the valence band and makes the recombination energy transfer mechanism hardly possible. Thus, we deal with a system where intrinsic electronic excitations predominantly relax via exciton or defects without transferring energy to Nd³⁺ ions.

The time profile of the Nd³⁺ 5d–4f emission at RT, monitored at 257 nm and excited at 164 nm, demonstrates a single exponential behaviour with an approximate lifetime of 14 ns (see the inset in Fig. 1), that agrees well with Nd³⁺ 5d–4f emission lifetime observed in other single crystal fluorides (14 ns in BaY₂F₈ [35], 15.3 ns in SrF₂, 12.3 ns in BaF₂ and 17.7 ns in CaF₂ [36]). We note that the time profile in Fig. 1 is shown just within 200 ns (not in a whole time scale of 480 ns) for better representation. The lifetime remains nearly the same when the sample is cooled down to 8 K (see the inset in Fig. 2), suggesting no thermal quenching for the Nd³⁺ 5d–4f emission within the temperature range of 8–300 K. In

addition, it is worth noting that the Nd^{3+} 5d–4f emission decay curves do not reveal any significant rise time within the time resolution capabilities of the synchrotron setup (better than 1 ns), indicating that excited Nd^{3+} 4f²5d¹ states do not experience any thermally assisted population of the emitting level.

Finally, it should be pointed out that no significant influence of codoping with Na^+ (added as a charge compensator to eliminate defect-distorted Nd_{Ba} sites) in BMF:Nd^{3+} was observed neither in the emission spectra nor in the decay curves. A small difference was observed in a time-integrated excitation spectrum of the Na^+ co-doped crystal. The difference, however, is just in a relative intensity of the spectral features not in their spectral positions (Fig. 3). The different relative intensity of the spectral features probably originates from a saturation effect that depends on thickness, orientation and surface quality of the crystal.

4. Conclusions

In this study we have shown that BaMgF_4 is an excellent host for fast and efficient 5d–4f luminescence of Nd^{3+} ions. The Nd^{3+} 5d–4f emission has been shown to decay with a lifetime of 14 ns while experiencing no thermal quenching of the luminescence within the temperature range 8–300 K. The host-to-dopant energy transfer has been found to be inefficient. Nevertheless, an overall spectroscopic and dynamic characteristics recorded for BMF:Nd^{3+} single crystal in combination with its nonlinear optical properties suggest this system can be a good candidate for the development of optical devices active in the VUV–UV regions, including tunable VUV–UV solid state lasers.

Acknowledgements

The authors wish to acknowledge Dr. A. Kotlov for help during the measurements at the SUPERLUMI setup at HASYLAB, DESY (Hamburg). The work has been partially supported by Spanish MICINN MAT2010-17443 and Comunidad de Madrid 2009MAT/1756.

References

- [1] K. Shimamura, E.G. Villora, K. Muramatsu, N. Ichinose, J. Cryst. Growth 275 (2005) 128.
- [2] E.G. Villora, K. Shimamura, K. Sumiya, H. Ishibashi, Opt. Express 17 (2009) 12362.
- [3] L. Mateos, M.O. Ramírez, I. Carrasco, P. Molina, J. Galisteo, E.G. Villora, C. de las Heras, K. Shimamura, C. López, L.E. Bausá, Adv. Funct. Mater. 24 (2013) 1509.

- [4] S. Janssens, G.V.M. Williams, D. Clarke, J. Lumin. 134 (2013) 227.
- [5] S. Kück, I. Sokolka, M. Henke, T. Scheffler, E. Osiac, Phys. Rev. B: Condens. Matter 71 (2005) 165112.
- [6] M. Yamaga, T. Imai, N. Kodama, J. Lumin. 87–89 (2000) 992.
- [7] K.V. Ivanovskikh, A. Meijerink, F. Piccinelli, A. Speghini, E.I. Zinin, C. Ronda, M. Bettinelli, J. Lumin. 130 (2010) 893.
- [8] S.I. Omelkov, M.G. Brik, M. Kirm, V.A. Pustovarov, V. Kiisk, I. Sildos, S. Lange, S. I. Lobanov, L.I. Isaenko, J. Phys. Condens. Matter 23 (2011) 105501.
- [9] A.G. Petrosyan, G.O. Shirinyan, K.L. Ovanesyan, C. Pédrini, C. Dujardin, N. Garnier, S. Sowinski, P. Lecoq, A. Belsky, Nucl. Instrum. Methods Phys. Res., Sect. A 486 (2002) 74.
- [10] J.E. Muñoz Santiuste, H. Loro, R. Marino, P. Goldner, V. Vasiliev, E.G. Villora, K. Shimamura, P. Molina, M.O. Ramírez, L.E. Bausá, Phys. Rev. B: Condens. Matter 85 (2012) 184110.
- [11] R.W. Waynant, P.H. Klein, Appl. Phys. Lett. 46 (1985) 14.
- [12] M.A. Dubinskii, A.C. Cefalas, E. Sarantopoulou, S.M. Spyrou, C.A. Nicolaidis, R. Y. Abdulsabirov, S.L. Korableva, V.V. Semashko, J. Opt. Soc. Am. B: Opt. Phys. 9 (1992) 1148.
- [13] F. Gingl, Z. Anorg. Allg. Chem. 623 (1997) 705.
- [14] E.G. Villora, P. Molina, S. Álvarez, J.V. García-Santizo, M.O. Ramírez, K. Shimamura, L.E. Bausá, J. Appl. Phys. 107 (2010) 033106.
- [15] L. van Pieterse, M.F. Reid, R.T. Wegh, S. Soverna, A. Meijerink, Phys. Rev. B: Condens. Matter 65 (2002) 045113.
- [16] L. van Pieterse, R.T. Wegh, A. Meijerink, M.F. Reid, J. Chem. Phys. 115 (2001) 9382.
- [17] C.W.E. van Eijk, P. Dorenbos, R. Visser, IEEE Trans. Nucl. Sci. 41 (1994) 738.
- [18] N.M. Khaidukov, M. Kirm, S.K. Lam, D. Lo, V.N. Makhov, G. Zimmerer, Opt. Commun. 184 (2000) 183.
- [19] R.T. Wegh, W. van Klinken, A. Meijerink, Phys. Rev. B: Condens. Matter 64 (2001) 045115.
- [20] V.N. Makhov, N.Y. Kirikova, M. Kirm, J.C. Krupa, P. Liblik, A. Lushchik, C. Lushchik, E. Negodin, G. Zimmerer, Nucl. Instrum. Methods Phys. Res., Sect. A 486 (2002) 437.
- [21] S.C. Buchter, T.Y. Fan, V. Liberman, J.J. Zayhowski, M. Rothschild, E.J. Mason, A. Cassanho, H.P. Jenssen, J.H. Burnett, Opt. Lett. 26 (2001) 1693.
- [22] E. Hayashi, K. Ito, S. Yabashi, M. Yamaga, N. Kodama, S. Ono, N. Sarukura, J. Lumin. 119–120 (2006) 69.
- [23] N. Kodama, T. Hoshino, M. Yamaga, N. Ishizawa, K. Shimamura, T. Fukuda, J. Cryst. Growth 229 (2001) 492.
- [24] S. Watanabe, T. Ishii, K. Fujimura, K. Ogasawara, J. Solid State Chem. 179 (2006) 2438.
- [25] L.L. Kang, T.Y. Liu, Q.R. Zhang, L.Z. Xu, J. Synth. Cryst. 39 (2010) 1470.
- [26] P. Dorenbos, J. Lumin. 91 (2000) 155.
- [27] G.W. Rubloff, Phys. Rev. B: Condens. Matter 5 (1972) 662.
- [28] C. Jouanin, J.P. Albert, G. Gout, J. Phys. Fr. 37 (1976) 595.
- [29] K.S. Song, R.T. Williams, Self-Trapped Excitons, Springer-Verlag, Berlin-Heidelberg, 1996.
- [30] A.N. Belsky, J.C. Krupa, Displays 19 (1999) 185.
- [31] P. Dorenbos, J. Lumin. 108 (2004) 301.
- [32] P.A. Rodnyi, I.V. Khodyuk, G.B. Stryganyuk, Phys. Solid State 50 (2008) 1639.
- [33] C.-G. Ma, M.G. Brik, W. Ryba-Romanowski, H.C. Swart, M.A. Gusowski, J. Phys. Chem. A 116 (2012) 9158.
- [34] A.H. Krumpel, E. van der Kolk, D. Zeelenberg, A.J.J. Bos, K.W. Kramer, P. Dorenbos, J. Appl. Phys. 104 (2008) 073505.
- [35] J. Pejchal, K. Fukuda, M. Nikl, N. Kawaguchi, Y. Yokota, T. Yanagida, A. Yoshikawa, IEEE Trans. Nucl. Sci. 59 (2012) 2177.
- [36] E. Radzhabov, V. Nagirnyi, M. Kirm, E. Prosekina, IEEE Trans. Nucl. Sci. 59 (2012) 2074.